

# RESERVE COPY.

## PATENT SPECIFICATION

NO DRAWINGS

1026.978



1026.978

Date of Application and filing Complete Specification March 12, 1963.

No. 9822/63.

Application made in Germany (No. Sch 31224 Iva/30h) on March 30, 1962.

Complete Specification Published April 20, 1966.

© Crown Copyright 1966.

Index at acceptance: —D1 B2A1

Int. Cl.: —D 06 p

### COMPLETE SPECIFICATION

#### Method of Dyeing Hair

We, SCHWARZKOPF VERWALTUNG G.M.B.H., a body corporate organized and existing under the laws of Germany, of Hohenzollernring 127—129, Hamburg-Altona, Germany, trading as HANS SCHWARZKOPF CHEMISCHE FABRIK, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Hair-dyeing processes are known using neutral or slightly alkaline compositions containing dye intermediates which can be developed into dyes by oxidation and, in addition, one or more diamino-pyridines, preferably 2,3-diaminopyridine, 2,6-diaminopyridine and/or substitution products thereof.

In accordance with the present invention it has been found that if hair is treated with a neutral or slightly alkaline composition, for instance an ammoniacal solution, cream or paste, containing 2,5-diaminopyridine with or without additional known oxidation dyes, a pure oxidation red of surprisingly high moisture resistance can be obtained.

Such red shades are needed for example for fashionable tinting of dark hair, to produce fashionable blonde shades, as a complementary colour to unsightly hair with a touch of green and for giving nuances to any other hair shades.

It is already known to produce yellow to orange shades in hair by means of nitrobenzene derivatives, for example with 2-amino-4-nitrophenol, 4-amino-2-nitrophenol, 4-nitro-1,2-phenylenediamine, 2-nitro-1,4-phenylenediamine or 4,6-dinitro-2-aminophenol. These, however, are direct dyeing dyes and not oxidation dyes. Owing to their water-solubility the moisture-resistance of the shades obtained with them, and particularly their resistance to shampooing, is

unsatisfactory in practice. Another disadvantage is that if the hair is of varying porosity they dye it unevenly.

It is also known that blue-red oxidation hair-shades can be obtained by combining  $\alpha$ -naphthol with p-toluylene diamine or m-phenylenediamine with p-aminophenol. But in either case only blue-red shades are produced, not pure red ones. Moreover relatively narrow limits are imposed on the richness of the shades obtained by using  $\alpha$ -naphthol, owing to its poor solubility and its molecular size.

The 2,5-diaminopyridine used in accordance with the invention is distinctive in being physiologically innocuous; even persons who tend to be allergic to "para" compounds can tolerate this compound without any reaction. In conjunction with other easily tolerable compounds such as 2,6-dihydroxypyridine, 2,3-diaminopyridine and 2,6-diaminopyridine, physiologically harmless hair tints can be obtained in virtually all the fashionable and natural shades, *inter alia* blonde and brown.

The 2,5-diaminopyridine compound may also be combined with aromatic amines and/or phenols known as initial dye intermediates, such as p-phenylenediamine, p-toluylenediamine, m-phenylenediamine, m-toluylenediamine, p-aminophenol, p-amino-N-dimethylaniline, 4,4'-diaminodiphenylamine, m-diaminoanisole, m-diethylaminophenol, 2,3-diaminopyridine, 2,6-diaminopyridine, m-aminophenol, o-aminophenol,  $\alpha$ -naphthol, 2,6-dihydroxypyridine, resorcin, pyrocatechoic acid, pyrogallol, hydroquinone, phloroglucine or 2,7-dihydroxynaphthalene.

In many cases the action of atmospheric oxygen is sufficient to develop the dyes from the initial dye products, although the tinting process can be accelerated by adding a

chemical oxidant, preferably hydrogen peroxide or compounds thereof.

The following examples illustrate the method according to the invention using simple dye solutions. In practice, however, such solutions will generally contain a variety of other additives such as thickeners, moisteners, stabilisers and emulsified fats such as are quite conventional in the art of hair dyeing.

#### EXAMPLE I

3.0 g. 2,5-diaminopyridine hydrochloride are dissolved in 4.0 g. of 25% ammonia solution and 93.0 g. water.

When applied to bleached hair, left to act for 30 minutes, rinsed out and the hair dried, this solution produces a pleasant red shade of high moisture-resistance.

#### EXAMPLE II

70 g. of the solution used in Example I are mixed with 30 ml. 6% hydrogen peroxide and the mixture is allowed to act on the hair. After 20 minutes at room temperature the mixture is washed out and deep red is obtained.

#### EXAMPLE III

0.4 g. 2,5-diaminopyridine and 0.4 g. p-toluylenediamine are dissolved in 4.0 g. of 25% ammonia solution and 95.2 g. water.

70 ml. of this solution are mixed with 30 ml. 6% hydrogen peroxide and applied to the hair. After acting on the hair for 20 minutes the mixture is washed out. A chestnut-brown shade is obtained.

#### EXAMPLE IV

0.2 g. 2,5-diaminopyridine and 0.2 g. 4-amino-diphenylamine are dissolved in 4.0 g. of 25% ammonia solution and 95.6 g. water.

The solution is made as in Example III and dyeing is effected under the same conditions. A fair chestnut shade is obtained.

#### EXAMPLE V

0.4 g. 2,5-diaminopyridine and 0.4 g. 4,4'-diaminodiphenylamine are dissolved in 4.0 g. of 25% of ammonia solution and 95.2 g. water.

The solution is made as in Example III and dyeing is effected under the same conditions. The solution dyes the hair violet.

#### EXAMPLE VI

0.4 g. 2,5-diaminopyridine and 0.4 g. o-aminophenol are dissolved in 4.0 g. of 25% ammonia solution and 95.2 g. water.

The solution is made as in Example III and dyeing is effected under the same conditions. The resultant shade is auburn.

#### EXAMPLE VII

0.5 g. 2,5-diaminopyridine and 0.5 g.  $\alpha$ -

naphthol are dissolved in 4.0 g. of 25% ammonia solution and 95.0 g. water.

The solution is made as in Example III and dyeing is effected under the same conditions. The hair is tinted red-violet.

#### EXAMPLE VIII

0.6 g. 2,5-diaminopyridine and 0.4 g. 2,6-diaminopyridine are dissolved in 4.0 g. of 25% ammonia solution and 95.0 g. water.

The solution is made as in Example III and dyeing is effected under the same conditions. It tints the hair orange.

#### EXAMPLE IX

0.5 g. 2,5-diaminopyridine and 0.5 g. 2,6-dihydroxypyridine are dissolved in 4.0 g. of 25% ammonia solution and 95.0 g. water.

The solution is made as in Example III and dyeing is effected under the same conditions. It tints the hair blue-violet.

#### EXAMPLE X

1.5 g. 2,5-diaminopyridine and 0.5 g. 2,6-dihydroxypyridine are dissolved in 4.0 g. of 25% ammonia solution and 94.0 g. water.

The solution is made as in Example III and dyeing is effected under the same conditions. A dark-brown shade is obtained.

#### EXAMPLE XI

0.3 g. 2,5-diaminopyridine, 0.2 g. 2,3-diaminopyridine and 0.2 g. 2,6-diaminopyridine are dissolved in 4.0 g. of 25% ammonia solution and 95.3 g. water.

The solution is made as in Example III and dyeing is effected under the same conditions. It tints the hair a deep blonde shade.

#### EXAMPLE XII

0.4 g. 2,5-diaminopyridine, 0.2 g. 2,3-diaminopyridine, 0.2 g. 2,6-diaminopyridine and 0.2 g. 2,6-dihydroxypyridine are dissolved in 4.0 g. of 25% ammonia solution and 95.0 g. water.

The solution is made as in Example III and dyeing is effected under the same conditions. A deep ash blonde shade is obtained.

#### WHAT WE CLAIM IS:—

1. A method of dyeing hair in which the hair is treated with a neutral or slightly alkaline composition containing 2,5-diaminopyridine followed by oxidation to develop the dye.

2. A method according to Claim 1, in which the 2,5-diaminopyridine is used in an ammonia solution, cream or paste.

3. A method according to Claim 1, in which the composition also contains a compound known as an oxidation hair dye.

4. A method according to Claim 3, in which the known hair dye is an aromatic amine and/or phenol.

5. A method according to Claim 4, in

- which the known hair dye is p-phenylenediamine, p-toluylenediamine, m-phenylenediamine, m-toluylenediamine, p-aminophenol, p-amino-N-dimethylaniline, 4,4'-diaminodiphenylamine, m-diaminoanisole, m-diethylaminophenol, 2,3-diaminopyridine, 2,6-diaminopyridine, o-aminophenol, m-aminophenol,  $\alpha$ -naphthol, 2,6-dihydroxypyridine, resorcin, pyrocatechoic acid, pyrogallol, 10 hydroquinone, phloroglucine or 2,7-dihydroxynaphthalene.
- 5
6. A method according to any one of the preceding claims, in which the 2,5-diaminopyridine and known oxidation dye, if present, are developed by means of a chemical oxidant. 15
7. A method according to Claim 6, in which the chemical oxidant used is hydrogen peroxide.
8. Hair when dyed by a method claimed in any one of the preceding claims. 20

For the Applicants,  
D. YOUNG & CO.  
Chartered Patent Agents,  
9, Staple Inn,  
London, W.C.1.